

PROCESSING OF SPENT NICKEL CATALYST FOR FAT RECOVERY¹

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SUMMARY

Spent nickel catalyst (SNC) has the potential of insulting the quality of the environment in a number of ways. Its disposal has a pollution effect. Optimum recovery of fat from SNC, could save the environment and reduce the oil loss. Hexane has been the solvent of choice for oil extraction. Alternative solvents considered to have been safer have been evaluated. Hexane, isopropanol, ethanol and heptane were examined using soxhlet extraction. While hexane is more efficient in oil recovery from SNC, isopropanol proved to be very good in clear separation of oil from waste material and also provides high solvent recovery compared to other solvents. Isopropanol extraction with chill separation of miscella into lower oil-rich phase, and an upper, solvent-rich recyclable phase save much energy of vaporization for distilling. An aqueous extraction process with immiscible solvent assisted was tested. Solvent like hexane added to SNC, and water added later with continuous stirring. The mixture was stirred for about 30 minutes, prior to centrifugation. Aqueous process extracted less amount of oil compared to solvent extraction.

Keywords: SNC; Soxhlet; Isopropanol; Solvent extraction; Fat

RESUMO

PROCESSAMENTO DO CATALIZADOR NÍQUEL USADO PARA A RECUPERAÇÃO DE GORDURAS. O catalizador Níquel usado(SNC) apresenta potencial de deterioração da qualidade do meio ambiente de diversas formas. Seu resíduo tem efeito poluidor. Uma ótima recuperação da gordura do SNC poderia salvar o ambiente e reduzir as perdas de óleo. Hexano é o solvente mais utilizado na extração de óleo. Um solvente alternativo relacionado com segurança está sendo avaliado nesse trabalho. Hexano, isopropanol, etanol e heptano foram examinados utilizando o método de extração por soxhlet. Enquanto o hexano se mostrou mais eficiente na recuperação de óleo do SNC, o uso do propanol se mostrou muito bom na recuperação do óleo, do material do descarte e também proporcionou altas taxas de recuperação de solvente quando acompanhado com outro solvente. A extração com isopropanol com separação a frio na miscela pobre em óleo pouparia uma grande energia de vaporização na destilação. Um processo de extração aquoso com solvente imiscível foi usado como controle. Solventes como hexano adicionados ao SNC e água adicionada posteriormente com agitação contínua. A mistura foi agitada por cerca de 30 minutos, antes da centrifugação. O processo de extração aquoso extrai menor quantidade de óleo, comparado com a extração por solvente.

Palavras-chave: SNC; Soxhlet; Isopropanol; extração por solvente; gordura.

1 – INTRODUCTION

In the edible oil industry, nickel catalyst is used for hydrogenation of liquid oil to modify its physicochemical properties into semisolid plastic fats. The nickel catalyst

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is deactivated in due course of time and becomes a waste material [4,16]. It should be deposited in a disposal site strictly controlled so that groundwater, air and land are adequately protected and are not exposed to harmful amount of toxics. To prevent the contamination of groundwater and other pollution activity, a landfill must provide extremely reliable protection. So, it looks like the disposal of SNC will be expensive [4,12].

The SNC contains about 40 - 50% fat which is a valuable amount to recover for reuse as "edible" or for soap if it is not of good quality. In addition to 9 – 12% nickel as well as filter aid which can be recovered and re-used in the fat industry [10,15]. In this instance environmental pollution caused by fat processing waste could be reduced by appropriate recovery of these waste materials [4,8]. The impact of used catalyst treatment on environmental conservation was reviewed by HONGO [6].

In oil extraction, hexane is the most expensive solvent used. Since n-hexane is considered to be a hazardous air pollutant, interest in alternatives to hexane as an extraction solvent has been stimulated. Isopropanol, ethanol, heptane in addition to hexane have been tested in oil extraction from SNC in this research.

Extraction of oil from oilseed flour, which is close to characteristics of SNC, has been done with aqueous-enzymatic process during the last three decades [18]. However no attempt has taken place to extract oil from SNC by aqueous process.

Investigation is undertaken to determine the feasibility of recovering of fat and oil by aqueous process as well as by solvent extraction from SNC. Isopropanol extraction with chill separation of miscella to save the energy of vaporization for distilling was tested. To find a better alternative for hexane in the extraction of oil from SNC is one of the objects of this study.

2 – MATERIALS AND METHODS

2.1 – Materials

Samples of SNC were obtained from Jahan Vegetable Oil Co. plant in Karaj, Iran. The samples were removed warm directly after filtration and sealed into airtight containers and were stored after one hour at - 20°C until extraction. All chemicals and solvents used were of analytical reagent or above of E. Merck (Germany) or Fluka (Switzerland). They were used as received.

2.2 – Procedures and apparatus

The extraction of fats from SNC was done by a soxhlet extractor of 25 gin for different periods (2-8h) with hexane

and isopropanol as solvents. The solvent to SNC ratio in the extractor was 10:1 and 12:1 (WIV) with hexane and 12:1 with isopropanol and other solvents. Ethanol and heptane were examined for a 4 hour period only. The temperatures in the extractor were around 65°C for hexane, 78°C for isopropanol and ethanol and 88°C for heptane. The miscella obtained was distilled off on a water bath and hence under reduced pressure for recovery of solvent [15] except heptane, which was distilled with out water bath. The solvent free oil is stored at -20°C until use. For chill separation isopropanole miscalls were chilled to about 5°C in a refrigerator over-night to separate into lower oil phase and upper isopropanol phase by gravity. The lower phase was removed by decanting.

The aqueous extraction was done with 10gm of SNC with 10 and 15ml of hexane as assisted solvent and stirred at about 40CC on heater-stirrer (IKA MAG, Jance & Kankel, Germany) for 20 minute and then 40ml water was added with continuous stirring for another 30 minutes. Hexane was distilled for recovery before the miscella centrifuged. The remaining material was centrifuged with a laboratory centrifuge (Hermle ZK 380, Germany) with 9000rpm for 40 min. at a temperature of 38°C, and miscella was separated into three layers of solids, water and oil. The top layer was pipelted away for oil determination.

Recovery of nickel from SNC for estimation was done by the digestion of the de-fatted material (10gin) with 1:5 ratio (WIV) of 2 M sulphuric acid for a duration of two hrs at 95°C. Then it was filtered and the filtrate was treated with nitric acid at 100°C for 90mm. to convert iron from ferrous to ferric form. The solution was then neutralized with 2N sodium hydroxide to pH 6 to precipitate the ferric hydroxide, which was removed by filtration. The filtrate was analyzed for its nickel content.

2.3 – Analysis

The free fatty acid (FFA) content in the oil and iodine values were determined according to the AOCS procedures [11]. The spent catalyst was analyzed for its moisture content by weight loss from a 10gm sample dried at 100 + 2°C for two hrs. [10] The fat content was determined by the gravimetric method. Nickel content was determined gravimetrically using dimethylglyoxime and volumetrically with EDTA [17]. Iron was determined gravimetrically by weighting the dry ferric hydroxide and volumetrically with EDTA [17]. Melting points were determined using the capillary tube method. Fatty acid composition of the fat was determined by transesterification with sodium methoxid and analysis of the methyl esters by gas chromatography using a Varian Star 3400 CX GC equipped with flame ionization detector.

3 – RESULTS AND DISCUSSION

The fat from SNC was extracted with soxhlet using hexane, isopropanol, ethanol and heptane as solvent. The composition of the SNC is presented in *Table 1*. The appreciable proposition of 2.3% iron impurity in the SNC most probably due to the use of mild steel hydrogenation

vessel. The nickel content of 9.9% is less than half of the parent catalyst, which was 23%. The relatively high values of standard deviation of oil perhaps is the result of changing the amounts of fresh catalyst used for hydrogenation in some batch of the process to speed up the hydrogenation. Another cause could be the tendency of solvent to channel and fine particles to pack [13] and that may make a different in oil extracted by solvent. The positive error (0.4%) in *Table 1* may be due to the presence of little solvent in oil [3].

TABLE 1. Composition of Spent Nickel Catalyst ^a

Constituent	content (%) b
Moisture	1.71 – 0.12
Iron	2,31 – 0.15
Nickel	9,91 – 1.60
Inert material	42.5 – 12.20
Fat	4.01 – 3.56

^a Fat extracted with hexane for a period of 4 hrs using soxhlet extractor. ^b Average of six determination from 3 samples, with standard deviation.

It has been noticed that if the fresh SNC is processed a white fat is recovered otherwise light yellow colour fat is obtained due to oxidation. While in the first case the quality of fat is such that it can be utilized for edible purposes, coloured fat can be used for the soap production. The characteristics of oil extracted from fresh SNC is shown in *Table 2*. The low iodine value (50) compared to the fat produced by catalyst hydrogenation (75-80), is perhaps due to the accumulation of more hydrogenated fat on the catalyst. It seems that the low temperature (-20°C) and airtight container did not stop the oxidation of the fat, may be due to a high amount of heavy metal (iron) in the fat. *Table 3* shows the effect of time on FFA of the fat.

TABLE 2. Characteristics of fat extracted with two days with hexane from spent catalyst.

Item	Value
Free fatty acid	0.10
Iodine value	50
Melting point	51 ⁰ C

^a Average of three determinations.

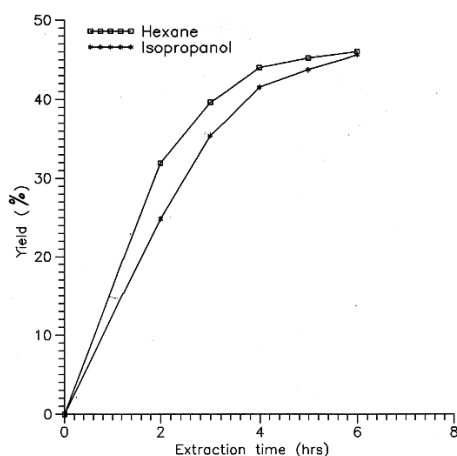
TABLE 3. The effect of time on the acidity of spent nickel catalyst fat. ^a

S. No	Time	FFA
1	2days	0.10
2	3 days	0.18
3	3 days	0.28
4	12 days	0.40
5	60 days	0.60

^a Average of three determinations.

For optimum recovery of fat from spent catalyst, experiment were performed in varying the amount of solvent used as well as extraction time. Increasing the amount of solvent (hexane) from 250ml to 300ml for 25gm of SNC resulted in increases in the amount of oil extracted from 40.1% to 44.0%. It seems that the ratio of 12:1 (VIW) of solvent to waste materials is the optimum ratio, as farther increase did not significantly increase the amount of extracted oil. There is also increase in solvent loss with the increasing of solvent ratio. That may be due to the increase in vapor process of the solvent.

Figure 1 shows that there are steady increases of fat yield with the increasing extraction times. The amount of fat extracted by hexane with different periods, was higher than that extracted by isopropanol, as isopropanol extract more slowly than hexane [9]. That is because hexane is a more efficient solvent for dissolving fat and its time interval for flashing the oil is 10min. while it is 14min. for isopropanol. For hexane, there are rapid increase in fat yield till 4hrs extraction time, while its small increase in fat yield continues in the case of isopropanol. The recovery of hexane after extraction and distillation was 88.5% and 85% for 2 and 6hrs extraction time, respectively. For isopropanol, it was 94.5% and 94% for 2 and 6hrs extraction times respectively.



Each value is average of at least 3 determination each of 3 samples.

FIGURE 1. Fat recovery (yield %) from 25gm of SNC with 300ml hexane or isopropanol with soxhiet as a function of the extraction time^a.

This difference is due to the difference in the heat of vaporization (cal/gm) which is 80 for hexane and 206 for isopropanol [2]. Another point in the comparison of hexane with isopropanol is the filterability. A clear separation of the oil from Nickel catalyst was achieved when isopropanol was used, while hexane did not provide that clear separation. This is in agreement with what Hennion reported [5]. In addition isopropanol is safer than hexane and is not considered hazardous like hexane [2,7]. In chill separation at about 5°C, the lower phase was removed by decanting containing 86.20% fat, while the solvent phase contained about 2.0% oil. Commercially the process can be hastened

with heat exchanger and centrifuges with less time and less energy than that used in vaporization [9].

Ethanol is less efficient than isopropanol in oil dissolution, but it has better filterability than that of hexane. Ethanol yield less oil than isopropanol yield in the same conditions (300 ml: 25 gm, for 4 hrs). Heptan is as good as ethanol but with poor filterability and required more energy than other the solvents tested here.

Fatty acid composition shown in Table 4, The fatty acid contains 3.40% polyunsaturated fatty acid which is the main target of fat oxidation. There are 46.20% saturation and 52.80% unsaturation. which can be fitted for soap preparation if can not use a for edible purposes.

TABLE 4. Fatty acid composition (%) of the oil before and after hydrogenation*

	Before hydrogenation a	Hydrogenated b	Recovered b
Fatty acid	(IV 130)	(IV=76)	(IV=50)
Palmitic C16:0	11.20	11.20	11.20
Stearic C18:0	4.00	9.10	35.00
Oleic C18:1	22.80	64.80	49.40
Linolenic C18:2	55.40	12.70	3.40
Linolenic C18:3	5.20	1.20	

^a data from the supplier of blend soybean, cotton seed, and sunflower seed oil.

^b data collected from CG analysis

* The remaining percentage is unknown fatty acid.

Aqueous extraction of oil is the alternative procedure in oil extraction as it is the most safe and not hazardous. The use of water alone did not give any result, in spite of strong mechanical agitation. It is due of strong clench of oil to the catalyst material. Hexane is used as immiscible assisted solvent with a ratio of 1:1 (WIV) of catalyst to solvent but it gives poor results. There is about 22% oil yield which is nearly half that of solvent extraction, with little fine particles which did not settle easily by gravity and the centrifuge (decanter) used in this study could not separate the fine particles from miscella effectively. Increasing the solvent ratio to 1:1.5 (WIV) did not increase the yield significantly. Hexane recovery in the aqueous process is about 90%.

These are few points of comparison between the aqueous and solvent processes. The solvent extraction is more efficient in oil extraction than that of aqueous extraction. The aqueous process is highly dependent on centrifuge which necessitate high maintenance and energy consumption, while solvent extraction does not required that.

4 – CONCLUSION

Environmental pollution caused by fat processing wastes could be reduced by appropriate recovery of edible and nonedible materials. Fat recovery from SNC with isopropanol as solvent serves this purpose. Isopropanol is safer and less toxic compared with hexane and having high ratio of recovery as well as having very good filterability. Chill-separation will save much energy used in heat of vaporization.

Recovered fat can be utilized for edible or soap purposes. Recovery of fat will increase the nickel content in the defatted material for the reprocess in nickel utilization. Aqueous extraction is a less efficient technique for SNC processing. It is advisable to leave a little amount of fat in the defatted materials, to help handling it easily as complete defatted is very fine powder difficult to handle and toxic (18).

5 – REFERENCES

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